$^{14}C/^{12}C$ VARIATIONS OF SAMPLES EXPOSED IN AIR ACCORDING TO CARBON STRUCTURE AND AIR TEMPERATURE

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ABSTRACT. Various carbon structures, including carbon nanofilament (CNF), single-wall carbon nanotube (SWCNT), multi-wall carbon nanotube (MWCNT), and pyrolytic graphite sheet (PGS), were exposed in air to determine how they vary according to carbon structure and air temperature. CNF is the carbon structure used in accelerator mass spectrometry (AMS) radiocarbon dating (Santos et al. 2007). When CNF and MWCNT were exposed in cold air (3 or –18 °C) for longer than 6 hr, their $^{14}C/^{12}C$ ratio increased ($>5 \times 10^{-14}$). When heated in an oven (200 or 250 °C) for longer than 12 hr, their $^{14}C/^{12}C$ ratio decreased. However, when SWCNT and PGS were exposed in air cooled to 3 °C for 12 hr, their $^{14}C/^{12}C$ ratio did not increase. This phenomenon is very curious, and is useful for the development of a storage method for carbon samples made by reduction reactions of CO_2.

INTRODUCTION

When samples are stored for accelerator mass spectrometry (AMS) measurement (Hong et al 2010b), contamination of the samples is of significant concern and interest. There are a variety of sample types in sample treatment procedures, including raw samples, chemically treated samples, and graphite samples reduced from CO_2 (Hong et al. 2010a). Graphite samples reduced from CO_2 are the final type of sample, and their measurement value is directly affected by their degree of contamination. Therefore, contamination of graphite samples reduced from CO_2 should be carefully controlled and thoroughly studied.

Sometimes, background samples for $^{14}C/^{12}C$ measurement are highly contaminated, with $^{14}C/^{12}C$ exceeding $\sim 5 \times 10^{-14}$ in our laboratory. We suspect that these phenomena are not common and do not occur in every laboratory. Various trials were performed, but no special conditions have been detected in our laboratory yet that would cause such results. While the understanding of high contamination phenomena remains limited, the special conditions resulting from high contamination rates in our laboratory are being investigated continuously. The results of this study will aid other researchers concerned with sample contamination.

Many factors of contamination have been identified, including air contamination, contamination of pelletizing tools, and contamination of tubes (PCR®, PCR-05-C) for the storage of pelletized background samples. To check for contamination by the pelletizing tools, we used unclean pelletizing tools for pelletizing background samples; however, the measurement values of these background samples were below 5×10^{-15}, and thus contamination of the pelletizing tools is not the main reason for high contamination of the background samples. Next, to check for contamination caused by the PCR tubes (PCR-05-C, 0.5 mL) for storing pelletized background samples, the $^{14}C/^{12}C$ ratio of the tubes was measured and the contamination level was found to be below 1×10^{-14}. Thus, it would be difficult for the tube to contaminate the samples up to $\sim 5 \times 10^{-14}$. Therefore, we suspected that air contamination was the likeliest factor that could account for the high degree of contamination.

To clarify the effects of air contamination, background samples were exposed to cold and hot air for various exposure times (6, 10, 12, and 24 hr), and their $^{14}C/^{12}C$ ratios were then measured. To assess whether various samples types, including carbon nanofilament (CNF), single-wall carbon nanotube

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(SWCNT), multi-wall carbon nanotube (MWCNT), and pyrolytic graphite sheet (PGS), could be contaminated by air, samples of each were also exposed to cold air, and their $^{14}C/^{12}C$ ratios were measured to check the degree of their contamination due to the air. CNF is a type of graphite sample used for AMS measurement that is reduced from CO_2 with H_2 and an Fe catalyst (Santos et al. 2007). SEM and TEM images of the background samples in Figure 1 show that their structure is similar to the CNF.

Figure 1 SEM images of samples used for AMS measurement: (a) 2000×; (b) 22,000×. (c) and (d) are TEM images of samples used for AMS measurement. The images show that their structure is similar to that of CNF.

EXPERIMENTAL PROCEDURE

Various types of carbon samples were used: background samples for AMS measurement and CNF, SWCNT, MWCNT, and PGS samples. Background samples were further classified into 2 types. One type was contaminated, with high $^{14}C/^{12}C$ ratios measured. The other type was not contaminated and therefore had lower $^{14}C/^{12}C$ ratios. For pyrolytic graphite sheets (PGS, Panasonic) purchased several years ago, the initial $^{14}C/^{12}C$ value had been about 1×10^{-15}. Carbon nanofilaments (CNFs, Carbon Nano-material Technology Co. Ltd. [CNT]), single-wall carbon nanotubes (SWCNTs, CNT), and multi-wall carbon nanotubes (MWCNTs, CNT) purchased recently were also prepared.

All of the background samples composed of graphite and Fe were pressed in a target holder and their pressed surface gleamed slightly. However, when the background samples were used for temperature experiments, as measured background samples were used, their surfaces were not clean and had scratches caused by the cesium ion beam. Two sets of SWCNT, MWCNT, and PGS samples were pressed in the target holder without Fe and 2 sets of CNF mixed with Fe were also pressed in the target holder. Their surfaces did not gleam. One set of samples was used for measuring their original values and the other set was used for measuring the change in value after temperature experiments. All of the samples were inserted and stored in PCR® tubes (PCR-05-C).

The 4 background samples with high ratios of ^{14}C/^{12}C were placed in an oven and exposed to hot air. Conditions of the experiment are listed in Table 1. Taking caution to limit the air exposure, the samples were equipped in the AMS and the ^{14}C/^{12}C ratios of the samples were measured.

Table 1 Experimental conditions are listed. ^{14}C/^{12}C ratios of before and after heating samples are also presented. After heating, the ^{14}C/^{12}C ratios of all samples decreased.

Carbon structure (ID)	Original ^{14}C/^{12}C	Changed ^{14}C/^{12}C	Temp (°C)	Time (hr)
CNF (TBg110236)	$(2.3840 \pm 0.8418)10^{-14}$	$(8.2424 \pm 1.1430)10^{-15}$	200	24
CNF (TBg110237)	$(2.5144 \pm 0.0812)10^{-14}$	$(8.3274 \pm 0.0931)10^{-15}$	200	24
CNF (TBg110229)	$(1.6031 \pm 0.0810)10^{-14}$	$(9.3159 \pm 1.3045)10^{-15}$	200	12
CNF (TBg110181)	$(2.0711 \pm 0.1472)10^{-14}$	$(3.9534 \pm 0.9884)10^{-15}$	250	12
CNF	$(1.3050 \pm 0.0764)10^{-13}$	$(1.9650 \pm 0.1189)10^{-14}$	200	12
MWCNT	$(1.1413 \pm 0.0775)10^{-13}$	$(1.6037 \pm 0.2224)10^{-14}$	200	12

The 3 background samples having low ^{14}C/^{12}C values were placed in a refrigerator and exposed to cold air. Two samples for each PGC, CNF, SWCNT, and MWCNT were prepared. Four out of the 8 samples were placed in a refrigerator and exposed to cold air, and the others were measured without any treatment. The details of the experiment conditions are listed in Table 2. Again, taking caution to limit air exposure, the cooled samples were equipped in the AMS, and the ^{14}C/^{12}C ratios of the samples were measured.

The 2 samples of CNF and MWCNT with high ^{14}C/^{12}C values that had been placed in the refrigerator were then placed in an oven set at 200 °C for 12 hr. The conditions of this experiment are also listed in Table 2. Taking caution to limit air exposure, the samples were equipped in AMS and the ^{14}C/^{12}C ratios of the samples were measured.

RESULTS AND DISCUSSION

From the data in Table 1 and Figure 2, it can be seen that the ^{14}C/^{12}C ratios of the heated background samples, the heated MWCNT, and the heated CNF were reduced. When the temperature was higher and the heating time was longer, the degree to which the ^{14}C/^{12}C ratios were reduced increased. After the MWCNT and CNF with higher ^{14}C/^{12}C ratios were heated in air at 200 °C for 12 hr, their ^{14}C/^{12}C ratios decreased further.

From these phenomena, it can be inferred that materials causing high contamination in the samples can easily reduced from the samples when subjected to high temperature, and that it takes more than 12 hr for the contaminants to be removed from the samples. Gases can be sensitive to temperature in terms of ease of removal from a given sample, whereas solids such as fine particles are not easily forced from the sample interior, and the speed of removal is not sensitive to temperature in the latter case. Therefore, there is a high possibility that the contaminant material is a gas such as CO_2, CO, or CH_4 (Chen et al. 2005).

From the data in Table 2 and Figure 3, the trends for variation of ^{14}C/^{12}C ratios of the cooled samples differ according to the carbon structures. After exposure to cold air in the refrigerator, the ^{14}C/^{12}C ratios of the background samples (CNF structure), the CNF and MWCNT, became very high, but the $^{14}C/^{12}C$ ratios of the PGS and SWCNT samples exposed to cold air did not change considerably.

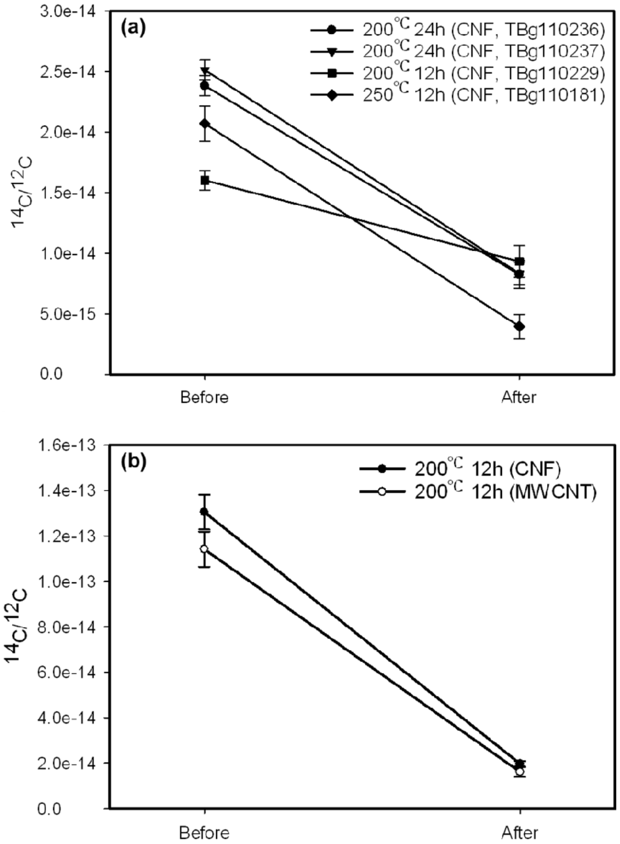

Figure 2 After heating the samples, $^{14}C/^{12}C$ ratios in all samples decreased

Table 2 Experimental conditions and $^{14}C/^{12}C$ ratios of samples before and after cooling. After cooling, the $^{14}C/^{12}C$ ratios of CNF and MWCNT samples increased, but the $^{14}C/^{12}C$ ratios of SWCNT and PGS samples did not change significantly.

Carbon structure (ID)	Original $^{14}C/^{12}C$	Changed $^{14}C/^{12}C$	Temp (°C)	Time (hr)
CNF (OBg110207)	$(3.8517 \pm 0.5015)10^{-15}$	$(7.9216 \pm 0.3074)10^{-14}$	3	18
CNF (TBg110279)	$(1.6094 \pm 0.1390)10^{-14}$	$(2.0346 \pm 0.0478)10^{-13}$	3	13
CNF (TBg110241)	$(1.8697 \pm 0.2267)10^{-15}$	$(4.7534 \pm 0.0733)10^{-13}$	–18	18
CNF	$(4.0776 \pm 0.4476)10^{-14}$	$(1.4892 \pm 0.0784)10^{-13}$	3	6
MWCNT	$(7.7916 \pm 2.1610)10^{-15}$	$(1.3375 \pm 0.1505)10^{-13}$	3	6
SWCNT	$(2.6408 \pm 0.7623)10^{-15}$	$(3.1473 \pm 0.6868)10^{-15}$	3	12
PGS	$\sim 110^{-15}$	$(1.6512 \pm 0.4005)10^{-15}$	3	12

The $^{14}C/^{12}C$ ratio of the background sample (TBg110241) was very high at $(4.7534 \pm 0.0733)10^{-13}$. Therefore, the $^{14}C/^{12}C$ ratio of a contaminant might be very high, and the contaminant may be a ^{14}C-enriched material. If it was not a ^{14}C-enriched material but rather a modern material, its adsorption

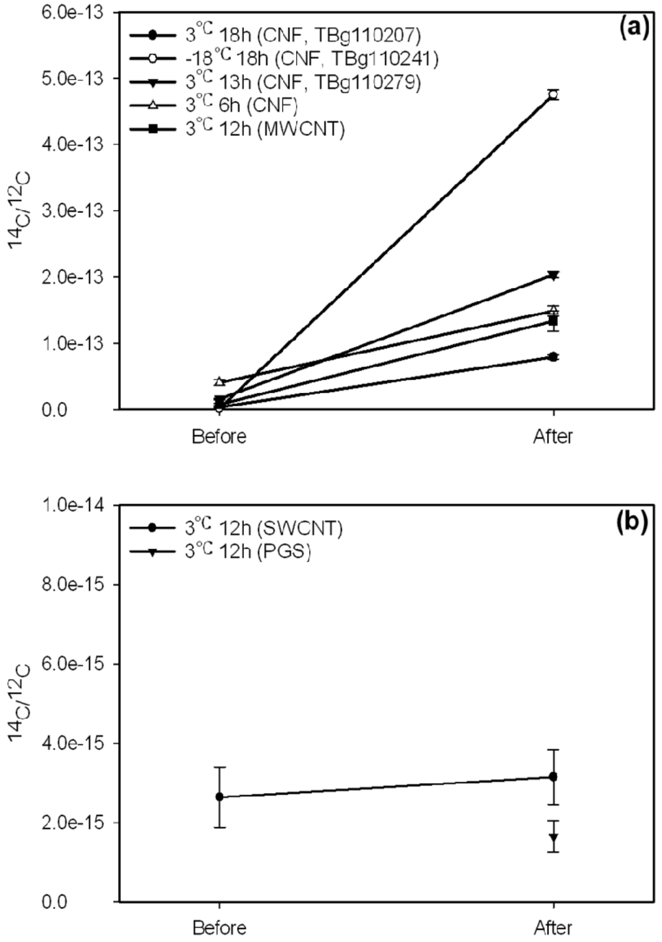

Figure 3 After cooling the samples, (a) shows that the $^{14}C/^{12}C$ ratios of CNF and MWCNT increased, but (b) shows that the $^{14}C/^{12}C$ ratios of SWCNT and PGS scarcely increased.

ratio might be ~50%, or only ^{14}C would be adsorbed selectively. All factors should be considered, but the material that has influenced the $^{14}C/^{12}C$ ratio of the background sample seems to have consistently been a ^{14}C-enriched material. However, it is thus far unclear why the PGS and SWCNT samples did not adsorb the ^{14}C-enriched materials, in contrast with the CNF and MWCNT samples.

CONCLUSION

From our experiment and results, we conclude that the contamination material's phase is gaseous because of its lengthy removal time (>12 hr) and its faster removal when exposed to higher temperature. Carbon structures also affect the amounts of contamination source gas that are adsorbed. The PGS and SWCNT samples hardly adsorbed the contamination source gas, whereas CNF and MWCNT samples adsorbed the contamination source gas very well. The molecular formula and identity of the contamination source gas and the reason and process of this contamination are important issues that need to be addressed in future research.

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REFERENCES

Chen L, Johnson K. 2005. Formation of odd-numbered cluster of CO_2 adsorbed on nanotube bundles. *Physical Review Letters* 94:125701, doi:10.1103/PhysRevLett.94.125701.

Hong W, Park JH, Kim KJ, Woo HJ, Kim JK, Choi HW, Kim DG. 2010a. Establishment of chemical preparation methods and development of an automated reduction system for AMS sample preparation at KIGAM. *Radiocarbon* 52(2–3):1277–87.

Hong W, Park JH, Sung KS, Woo HJ, Kim JK, Choi HW, Kim GD. 2010b. A new 1MV AMS facility at KIGAM. *Radiocarbon* 52(2–3):243–51.

Santos GM, Mazon M, Southon JR, Rifai S, Moore R. 2007. Evaluation of iron and cobalt powders as catalysts for ^{14}C-AMS target preparation. *Nuclear Instruments and Methods in Physics Research B* 259(1): 308–15.